

# Multi-Wavelength Laser Transmitter for the Two-Step Laser Time-of-Flight Mass Spectrometer

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**Abstract:** We are developing a multi-wavelength laser for the two-step laser time-of-flight mass-spectrometer (L2MS). The L2MS is designed to detect hydrocarbons in organically-doped analog minerals, including cryogenic Ocean World-relevant ices and mixtures for future astrobiology missions.

**OCIS codes:** (280.3640) Lidar; (300.6360) Spectroscopy, laser; (140.3580) Lasers, solid-state; (140.3070) Infrared and far-infrared lasers; (140.3540) Lasers, Q-switched; (140.3610) Lasers, ultraviolet

## 1. Introduction

Missions to diverse Outer Solar System bodies will require investigations that can detect a wide range of organics in complex mixtures, determine the structure of selected molecules, and provide powerful insights into their origin and evolution. Previous studies from remote spectroscopy of the Outer Solar System showed a diverse population of macromolecular species that are likely to include aromatic and conjugated hydrocarbons with varying degrees of methylation and nitrile incorporation [1]. In situ exploration of Titan's upper atmosphere via mass and plasma spectrometry has revealed a complex mixture of organics [2,3]. Similar material is expected on the Ice Giants, their moons, and other Outer Solar System bodies, where it may subsequently be deposited onto surface ices [4]. It is evident that the detection of organics on other planetary surfaces provides insight into the chemical and geological evolution of a Solar System body of interest and can inform our understanding of its potential habitability. We have developed a prototype two-step laser desorption/ionization time-of-flight mass spectrometer (L2MS) instrument by exploiting the resonance-enhanced desorption of analyte. We have successfully demonstrated the ability of the L2MS to detect hydrocarbons in organically-doped analog minerals, including cryogenic Ocean World-relevant ices and mixtures.

The L2MS instrument operates by generating a neutral plume of desorbed analyte with an IR desorption laser pulse, followed at a delay by a ultraviolet (UV) laser pulse, ionizing the plume. Desorption of the analyte, including trace organic species, may be enhanced by selecting the wavelength of the IR desorption laser to coincide with IR absorption features associated with vibration transitions of minerals or organic functional groups. In this effort, a preliminary laser developed for the instrument uses a breadboard mid-infrared (MIR) desorption laser operating at a discrete 3.475  $\mu\text{m}$  wavelength, and a breadboard UV ionization laser operating at a wavelength of 266 nm. The MIR wavelength was selected to overlap the C-H stretch vibrational transition of certain aromatic hydrocarbons, and the UV wavelength provides additional selectivity to aromatic species via UV resonance-enhanced multiphoton ionization effects [5]. The use of distinct laser wavelengths allows efficient coupling to the vibrational and electronic spectra of the analyte in independent desorption and ionization steps, mitigating excess energy that can lead to fragmentation during the ionization process and leading to selectivity that can aid in data interpretation [5,6].

## 2. Laser Transmitter for the L2MS Instrument

Our baseline approach to meet the L2MS requirement and provide a direct path for space is to leverage the successful spaceborne laser transmitter design from the lunar orbiter laser altimeter (LOLA) instrument. Since its launch in 2009, the LOLA instrument has sent well over 4 billion laser shots to the lunar surface for topographic mapping of the moon [7]. The LOLA laser design, which houses two laser transmitters on a single laser bench, fits well with the L2MS requirements and more importantly, provides a straightforward development path toward flight readiness.

In L2MS, a MIR desorption laser pulse is the leading pulse to transmit down the bore of the analyzer to the sample surface. After a time delay, an UV ionization laser pulse passes through a side view port to intersect the desorbed plume. The delay will be tuned to maximize the ion intensity of the species of interest at the detector, to account for small changes in geometry and position between samples. Typical delays ranged between 0.3 and 2  $\mu\text{s}$ .

Our MIR and UV laser transmitter designs for L2MS are based on the LOLA laser. As in LOLA, our two laser transmitters are both zig-zag Nd:YAG slabs side pumped by two 2-bar laser diode arrays at 808 nm to generate a fundamental wavelength of 1064 nm. The MIR laser is passively Q-switched with the output coupler replaced by a KTA crystal that is properly designed and parallel polished with end faces parallel to  $< 10$  arcseconds to form a monolithic intracavity optical parametric oscillator (iOPO). A 24-mm long KTA crystal is used in non-critical phase matching (NCPM) to eliminate the walk-off effect with a maximum effective nonlinear coefficient. The iOPO signal and idler wavelengths are 1534 nm and 3475 nm with output energies of 600  $\mu$ J and 210  $\mu$ J respectively, and with pulse repetition frequency (PRF) from single shot to 50 Hz.

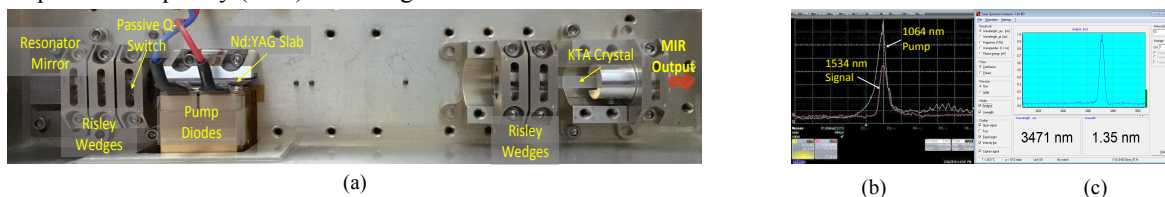


Figure 1. (a) MIR monolithic iOPO breadboard laser; (b) the temporal profile of the pump (1064 nm) wavelengths; and (c) the spectral profile of the idler wavelength for the iOPO laser transmitter.

The UV laser is electro-optic actively Q-switched to allow for much better timing control necessary to deliver the UV ionization pulse at a specified time delay from the MIR desorption pulse for the L2MS instrument. The 1064 nm laser is frequency doubled to 532 nm using a Type II critical phase matched (CPM) KTP crystal ( $\theta = 90.0^\circ$ ,  $\phi = 23.5^\circ$ ) operating near room temperature at  $27^\circ\text{C}$ . The 532 nm light is frequency doubled to 266 nm using a Type I BBO crystal ( $\theta = 47.7^\circ$ ) operating at room temperature ( $\sim 25^\circ\text{C}$ ). The initial breadboard performance was measured with the 1064 nm laser operating at a pulse energy of 1.64 mJ, PRF of 20 Hz and pulse duration of  $\sim 8.7$  ns and the UV laser pulse energy of 240  $\mu$ J at a PRF of 20 Hz and pulse duration of 6.7 ns. The overall optical-to-optical conversion efficiency for the 266 nm is approximately 15%.

The MIR and UV laser breadboards have been integrated with the L2MS prototype instrument for testing as shown in Figure 2. Successful coupling of the laser breadboards to the L2MS instrument enabled detection of caffeic acid encapsulated by a thin layer of water ice, for the first time. The mass spectrum of caffeic acid is shown in Figure 3 with the parent peak at 183 Da clearly displayed.

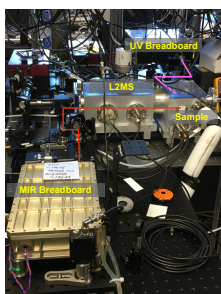


Figure 2. MIR and UV laser breadboards integrated with the L2MS instrument.

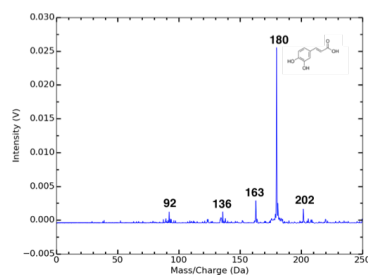


Figure 3. A mass spectrum of caffeic acid coated with water ice, measured at cryogenic temperatures.

### 3. Conclusions

We have demonstrated a simple, monolithic iOPO MIR laser and an UV laser that are based on a proven space flight laser architecture. The breadboard lasers have been successfully integrated with the L2MS instrument. We are in the process of designing and building a breadboard laser at 3.25  $\mu\text{m}$  for the L2MS instrument. We are also building a brassboard laser that houses both 3.25  $\mu\text{m}$  and 266 nm lasers on a single bench for integration with the L2MS instrument.

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